

bivalent sulfate a small collision diameter might explain part of the effect, but there is no reason to suppose that the factor which affects the halides is not also operative here. We are unable to say what this factor is.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE SPECIFIC HEATS OF FIVE ORGANIC LIQUIDS FROM THEIR ADIABATIC TEMPERATURE-PRESSURE COEFFICIENTS

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RECEIVED MARCH 5, 1932

PUBLISHED JULY 6, 1932

Introduction

Although the specific heats of liquids have been measured for nearly two centuries, there remains a distressing lack of agreement in the immense collection of numbers which have been reported to represent them. Because of the complexity of the correction factors which must be applied to the results of calorimetric determinations, it is not uncommon to find a divergence of ten per cent. between two investigations, although the estimated error of each is far below this value. While it is not at present possible to interpret the specific heats of most liquids even to this approximation, accurate knowledge of so fundamental a property must be ultimately both necessary and valuable. Any method other than the calorimetric should, therefore, be considered if it appears to offer a practical alternative.

From the first and second laws of thermodynamics, without further assumption, it follows that the adiabatic temperature-pressure coefficient of a system of heat capacity at constant pressure C_p is given by the expression

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{C_p} \left(\frac{\partial v}{\partial T}\right)_p$$

where T , p , s and v represent temperature, pressure, entropy and volume, respectively. Oersted¹ appears to have been the first to sense this relationship qualitatively, for he subjected water to a sudden pressure and attempted to measure a rise in its temperature. The formal derivation was carried out by Joule,² who experimentally proved the second law of thermodynamics by measuring the heat capacity, coefficient of thermal expansion and temperature-pressure coefficient of water and of fish oil. Several other investigations have subsequently dealt with the last of these quantities for solids, liquids and gases, although the majority do not lend themselves even to approximate calculation of specific heats, owing to the magnitude of the pressures employed. Creelman and Crocket,³

¹ Oersted, *Ann. chim. phys.*, **2**, 22, 192 (1823).

² Joule, *Phil. Mag.*, **17**, 364 (1859).

³ Creelman and Crocket, *Proc. Roy. Soc. Edinburgh*, **13**, 311 (1885).

Burton and Marshall,⁴ and Pushkin and Grebenschikov,⁵ for example, examined several liquids in this way, but used pressures always in excess of 300 atmospheres. Barus⁶ calculated the specific heat of water from interferometric data using the relationship derived by Joule. Finally, Dixon and Rodebush,⁷ following the republication of the equation by Lewis and Randall,⁸ used it to obtain the heat capacities of several liquid metals, and showed that an accuracy of 2% was attainable. Although it has several times been suggested that experiments of this kind are suitable for the determination of the specific heats of organic liquids, no searching test of the method appears hitherto to have been undertaken.

Experimental Method

It follows from the equation above that measurements of temperature and pressure suffice, if made under securely adiabatic conditions, to determine without correction the specific heat of a liquid, provided that its coefficient of thermal expansion is known. This may safely be taken from the literature, as it is by far the most readily measured of the various characteristic coefficients.

Of the several types of apparatus which suggest themselves for such an investigation the simplest was chosen. This consisted of a Geneva Society pump which was connected by means of a suitable valve system to a Bourdon type gage and to a pressure bomb of conventional design. The system was filled with castor oil, the connections and valves being of 1 cm. internal diameter to secure a rapid response to changes in pressure. The bomb contained a cell of the construction illustrated in Fig. 1. The wires from the copper-constantan thermoelement in the cell were passed out of the bomb through a hard rubber plug and suitable insulating tubing, leaks being effectively prevented by tightening the plug around the wires with a metal collar and gland nut. The other junction of the thermoelement system was immersed in a Dewar flask in the thermostat which contained the pressure bomb. Thus a zero potential difference was secured at the start of each measurement. The change of temperature following a change of pressure was ascertained by calibration of the thermoelement system. A White double potentiometer, one branch of which was connected to a control pair thermocouples outside the bath to indicate stray currents in the electrical system, was used to measure the change of potential corresponding to a given temperature difference. The standard practice with respect to shielding, insulation and prevention of stray currents due to bimetallic junctions in the circuit or motion of wires in the earth's magnetic field was observed. The precision of the results will be discussed below.

After calibrating the thermoelements and filling the cell with a suitable liquid, measurements were obtained by a uniform procedure. A difference of pressure was first established and, after temperature equilibrium had been reached, the reading of the gage was recorded, and the absence of stray currents in the galvanometer circuit con-

⁴ Burton and Marshall, *Proc. Roy. Soc. (London)*, **50**, 130 (1891).

⁵ Pushkin and Grebenschikov, *J. Chem. Soc.*, **123**, 2717 (1923); **125**, 2043 (1924).

⁶ Barus, *Pub. Carnegie Inst.*, **249**, 4 (1919).

⁷ Dixon and Rodebush, *THIS JOURNAL*, **49**, 1162 (1927).

⁸ Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York, 1923, p. 137.

firmed. An approximate calculation of the temperature drop to be expected from the release of the pressure was then made, and the potentiometer set with the circuit open to balance the corresponding potential difference. The pressure was then reduced to atmospheric by opening a valve, and the galvanometer circuit closed. Any difference between the calculated and the observed deflection was added to the potentiometer setting on the basis of a previous calibration of the galvanometer scale in microvolts per cm., and the result converted into temperature rise in degrees centigrade per bar (or per dyne $\times 10^6$).

Accuracy of Pressure Measurements.—The gage employed was calibrated in divisions of 0.33 atm. to 0.5% accuracy between 15 and 50 atm. The accuracy of the calibration was maintained by frequent checks against an absolute piston gage. The Bourdon gage method of determining pressures, although open to criticism on the ground that it does not permit the highest possible precision, was found both practical and accurate over the necessary range. Gages of several other types were tested and abandoned because of clumsiness, hysteresis or other serious defects.

Temperature.—The absolute temperature of the pressure bomb and the constant temperature side of the thermoelement pair was fixed as desired to $\pm 0.005^\circ$ by a conventional water thermostat. Owing to the thermal inertia of the bomb and its contents, and of the Dewar flask in which the constant temperature junction was fixed, fluctuations about the mean temperature in the bath were imperceptible in the electrical system. The value of the absolute temperature was read from a Bureau of Standards calibrated thermometer to 0.02° .

The difference between the temperature of the liquid before and after a measured change of pressure was a determining factor in the accuracy with which the specific heat could be calculated and was, therefore, given careful attention. Obviously the heat capacity of the junction used must be small enough so that it does not measurably alter the temperature assumed by the liquid after the adiabatic expansion. Also, the thermocouple must reach the temperature of the liquid within a few seconds after the change of pressure in order that the gradual return of the temperature of the liquid to that of the bath shall not measurably lower the observed temperature difference. Finally, since the adiabatic temperature-pressure coefficients of the liquid and of the glass walls into which the thermocouple is sealed are not identical, the length and surface of wire between the walls and the junction must be great enough in relation to the thermal conductivity of the wire to prevent the temperature of the walls from influencing that of the junction.

The optimum dimensions for wires and cell are, therefore, difficult if not impossible to calculate. They were ascertained experimentally by photographing the response of the galvanometer to the potential generated by a release of pressure and comparing this to its response to an instantaneous difference of potential of like magnitude. As expected, the two were not comparable if the thermoelement was too coarse, too near the

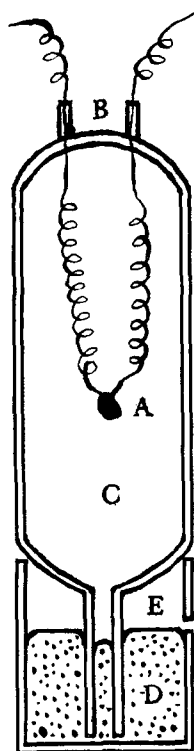


Fig. 1.—Cell for the measurement of the adiabatic temperature-pressure coefficient. The flattened thermoelement A is led out through the glass walls at B. The cell is entirely filled with liquid C, and mercury D employed to transmit the pressure impulse from the castor oil E.

glass walls, or immersed in too small a volume of liquid. In the experimental arrangement finally adopted and illustrated in Fig. 1, the response of the galvanometer to the release of pressure was as rapid as that to an instantaneous difference of potential, the maximum deflection being reached in both cases at the end of the period (5.4 sec.) of the critically damped galvanometer. The characteristic time-deflection curve before the maximum was almost identical in the two cases. The maximum deflection of the galvanometer persisted without measurable change for more than fifteen seconds after the critical period of the galvanometer had elapsed, showing that the slow return of the liquid to the temperature of the bath did not affect the accuracy of the observed temperature difference within a time interval easily sufficient to make the necessary measurements. This behavior is considered adequate proof that the release of the pressure and the response of the thermocouple were attained within a sufficiently short period, and that, therefore, the maximum deflection represented, except for an extremely slight correction due to work done on the galvanometer, the actual adiabatic temperature change corresponding to a given pressure.

The several thermoelements used were calibrated individually in exactly the temperature range for which they were employed by the usual method of immersing one junction in ice water and the other in a bath at the desired temperature and measuring potentiometrically the resulting difference in potential. All thermoelements used gave concordant potentials under similar conditions, the resulting temperature-potential function being essentially in agreement with that of Adams.⁹ The accuracy of the potentiometric system and the Beckmann thermometer employed defined the accuracy of the resulting calibration: the potential could be read to ± 0.05 microvolt, which gave an accuracy of $\pm 0.001^\circ$ to any single observation.

It may, therefore, be stated, to summarize the accuracy of the measurements, that the estimated absolute error of pressure was 0.5%, and of temperature 0.2% in the range used for investigation. It should be pointed out, however, that both pressure and temperature errors were apparently entirely random, and were, therefore, greatly reduced by multiplication of observations.

Purification of Materials

Benzene.—Starting with a guaranteed reagent grade the liquid was washed with sulfuric acid until no further darkening occurred, then repeatedly with dilute sodium hydroxide, and finally with water. It was then twice fractionally crystallized, dried with calcium chloride, and refluxed over phosphorus pentoxide. Finally it was twice fractionated, the second time from sodium wire. For the sample used the corrected b. p. was $80.20 \pm 0.05^\circ$, n_D^{20} 1.50132.

Toluene.—This was similarly washed with sulfuric acid, sodium hydroxide and water. It was dried with calcium chloride and refluxed with phosphorus pentoxide. Finally it was twice fractionated, the second time from sodium wire. For the sample used corrected b. p. was $110.50 \pm 0.05^\circ$, n_D^{20} 1.49630.

Carbon Tetrachloride.—A reagent grade was refluxed over mercury, washed with sulfuric acid, sodium hydroxide and water, dried with fused calcium chloride, and twice fractionated from freshly fused calcium chloride. For the sample used the corrected b. p. was $76.50 \pm 0.05^\circ$, n_D^{20} 1.46032.

Chloroform.—The accepted method of purification was found unsatisfactory for this substance owing to its partial oxidation to phosgene by washing with sulfuric acid, sodium hydroxide and water. Each sample was, therefore, merely fractionated from fresh fused calcium chloride, its boiling range and index of refraction being thus brought within the desired limits. Three samples from widely divergent sources were so pre-

⁹ Adams, "International Critical Tables," Vol. I, p. 57.

pared. They had boiling points and indices of refraction, respectively, of $61.15 \pm 0.05^\circ$, 1.44647; $61.15 \pm 0.05^\circ$, 1.44607; and $61.20 \pm 0.05^\circ$, 1.44598. Since no reason to distinguish between them was apparent, the results obtained with them are combined in the tables given below.

Normal Heptane.—This substance was obtained in a high state of purity from the Ethyl Gasoline Corporation. It was dried by fractionating from sodium wire. For the sample used the corrected b. p. was $98.35 \pm 0.05^\circ$, $n_D^{20} 1.38770$.

Numerical Constants.—Since the measurements reported below demonstrate that the quantity $(\partial T/\partial p)_s$ is effectively independent of pressure over a range of 0–30 atm., it follows that C_p is also sensibly constant over this range, and Equation 1 may be written in the form

$$C_p = \frac{\Delta p}{\Delta T} \left(\frac{\partial v}{\partial T} \right)_p \frac{T}{0.4185}$$

where pressure is now in bars, C_p in 15° calories per gram per degree (15° calorie = 4.185×10^7 ergs) and T in $^\circ\text{K}$. The values for $(\partial v/\partial T)_p$ were obtained in the extensive form by differentiation of the empirical density-temperature equations given in the "International Critical Tables." This coefficient must not, of course, be confused with the thermal coefficient of expansion, usually designated by α , which is expressed intensively. The volume-temperature differentials were chosen from a single source for the sake of uniformity. If they are subsequently revised a corresponding revision of the calculated specific heat may readily be made.

Typical Determination.—The reproducibility of measurements and

TABLE I

BENZENE 40°C . $(\partial v/\partial T)_p = 146.565 \times 10^{-5}$. 1 Microvolt = 0.02377°

Potential in mv.	ΔT in $^\circ\text{C}$.	Δp in bars	C_p in cal. ₁₅ $^\circ$
31.10	0.7392	28.61	0.4242
28.52	.6779	26.41	.4271
27.88	.6627	25.72	.4255
27.25	.6477	25.10	.4249
26.63	.6330	24.48	.4240
25.75	.6121	23.79	.4261
25.20	.5990	23.17	.4241
25.15	.5978	23.10	.4237
24.48	.5819	22.55	.4249
24.00	.5705	21.99	.4228
23.20	.5515	21.37	.4251
22.88	.5438	21.17	.4268
22.38	.5320	20.68	.4264
21.63	.5141	20.00	.4264
21.10	.5016	19.37	.4236
20.15	.4790	18.62	.4262
19.70	.4683	18.13	.4246
18.80	.4469	17.31	.4246
18.30	.4350	16.82	.4241
16.95	.4029	15.58	.4241
		Average	.4249

distribution of errors is best illustrated by quoting one series of observations which, in combination with a similar determination with a different thermoelement pair, led to the value for the specific heat of benzene at 40°. The concordance of experimental values was uniform in all determinations, and the results quoted are entirely typical. It will be noted that the temperature-pressure coefficient is sensibly independent of pressure over the observed range. The method is not, however, dependent upon this condition, for a correct value for the specific heat at atmospheric pressure may be obtained by extrapolation if necessary.

Summary of Results

Table II gives in condensed form the results obtained experimentally. Each value for the specific heat is determined by a set of measurements like that quoted in Table I, consisting of from 20 to 30 separate values. The calculated probable error of each value is always far below 0.1%. It has not been recorded, since systematic errors evidently may enter to at least this extent. At least two separate determinations of about twenty observations were made for any particular substance and temperature, always in different cells with different individually calibrated thermoelements.

TABLE II
SUMMARY OF MEASUREMENTS AND CORRESPONDING SPECIFIC HEATS

Temp., °K.	$(\partial T/\partial p)_s$ (av.) ^s deg. atm. ⁻¹	$(\partial v/\partial T)_p \times 10^3$ from "I. C. T."	Detns.	Average C_p per gram in cal. ₁₆ °
Benzene				
293.1	0.02396	1.3829	40	0.4095
303.1	.02503	1.4225	45	.4170
313.1	.02617	1.4657	42	.4246
323.1	.02732	1.5127	35	.4332
Toluene				
293.1	0.02191	1.2370	68	0.4007
303.1	.02272	1.2722	64	.4103
313.1	.02365	1.3125	45	.4201
323.1	.02470	1.3582	44	.4301
Normal Heptane				
293.1	0.02420	1.8113	49	0.5312
303.1	.02543	1.8661	43	.5383
313.1	.02681	1.9305	50	.5458
Carbon Tetrachloride				
293.1	0.02677	0.76393	42	0.2022
303.1	.02836	.78746	51	.2038
313.1	.03002	.81314	47	.2053
Chloroform				
293.1	0.02685	0.85157	62	0.2251
303.1	.02860	.88478	65	.2270
313.1	.03048	.92225	69	.2294

Discussion

The purpose of this investigation was entirely experimental, and no theoretical discussion will be attempted.

It is believed that the determinations quoted above are sufficiently accurate to fix the values of the various specific heats to better than 0.5%. Since no correction factors were necessary and the conditions of the measurements were thermodynamically satisfactory, it is difficult to estimate the systematic error. The agreement of the specific heats obtained with those of previous investigators is on the whole satisfactory, as Table III demonstrates. This is not the place to undertake a detailed analysis of such divergencies as occur.¹⁰

TABLE III
COMPARISON OF SPECIFIC HEATS WITH THOSE OF PREVIOUS INVESTIGATORS

Benzene					
Temp., °C.	R. and W. ^a	H., P. and D. ^b	"I. C. T." ^c	W. and D. ^d	Trehin ^e
20	0.4095	0.4088	0.4062	0.4080	0.4116
30	.4170	.4165	.4146	.4112	.4165
40	.4246		.4229	.4204	.4268
50	.4332		.4330	.4345	.4364
Toluene					
	R. and W. ^a	I. C. T. ^c	W. and D. ^d	Trehin ^e	
20	0.4007	0.3986	0.3899	0.4126	
30	.4103	.4067	.3985	.4243	
40	.4201	.4138	.4072	.4361	
50	.4301	.4208	.4158	.4459	
Normal Heptane					
	R. and W. ^a	W. and D. ^f	P., H. and T. ^g		
20	0.5312	0.5039	0.5262		
30	.5383	.5181	.5325		
40	.5458	.5323			
Carbon Tetrachloride					
	R. and W. ^a	W. and D. ^f	M. and McR. ^h		
20	0.2022	0.1990	0.2016		
30	.2038	.2033	.2019		
40	.2053	.2047	.2022		
Chloroform					
	R. and W. ^a	W. and D. ^f	Trehin ^e		
20	0.2251	0.2311	0.2276		
30	.2270	.2341	.2308		
40	.2294	.2372	.2341		

^a Richards and Wallace, this paper. ^b Huffman, Parks and Daniels, THIS JOURNAL, 52, 1547 (1930). ^c "International Critical Tables." ^d Williams and Daniels, THIS JOURNAL, 46, 1569 (1924). ^e Trehin, *Ann. phys.*, [9] 15, 246 (1921). ^f Williams and Daniels, THIS JOURNAL, 46, 906 (1924). ^g Parks, Huffman and Thomas, *ibid.*, 52, 1032 (1930). ^h Mills and McRae, *J. Phys. Chem.*, 15, 54 (1911).

¹⁰ A tabulation of all the first thermodynamic coefficients of the liquids here investigated from various sources is being compiled for separate publication by one of us.

Apart from calorimetric determinations, which show too great deviations among themselves to provide adequate comparison without attributing undue importance to a single investigation, only one direct check seems at present possible. The recent results of Shiba on the adiabatic and isothermal compressibilities¹¹ of benzene, toluene, chloroform, and carbon tetrachloride permit, with a knowledge of the coefficient of expansion, the calculation of the adiabatic temperature-pressure coefficient by the relationship

$$\frac{\left(\frac{\partial v}{\partial P}\right)_s - \left(\frac{\partial v}{\partial P}\right)_T}{\left(\frac{\partial v}{\partial T}\right)_P} = \left(\frac{\partial T}{\partial P}\right)_s$$

TABLE IV

COMPARISON OF THE MEASURED ADIABATIC TEMPERATURE-PRESSURE COEFFICIENT WITH THAT CALCULATED FROM THE RESULTS OF SHIBA

	Benzene			Toluene	
Temp., °C.	25	30	35	25	30
(dT/dP) _s exptl.	0.02449	0.02503	0.02560	0.02231	0.02274
(dT/dP) _s calcd.	.02376	.02431	.02474	.02093	.02112
	Carbon Tetrachloride			Chloroform	
Temp., °C.	25	30		25	30
(dT/dP) _s exptl.	0.02755	0.02836		0.02768	0.02857
(dT/dP) _s calcd.	.02671	.02718		.02672	.02785

Table IV illustrates the agreement between the values calculated by this means and those measured above. It may be seen that the agreement is far from satisfactory. Since the discordance is even greater if the previously accepted values for the specific heat are used to calculate the adiabatic temperature-pressure coefficient, it can hardly be attributed to errors in the measurements here reported. It seems probable, since Shiba's values for the adiabatic compressibility are in fair accord with those calculated from the velocity of sound, that the responsibility for this deviation must be attributed to his isothermal measurements, but the exact reason for it is not apparent from his communication.

Summary

The adiabatic temperature-pressure coefficients for 15 to 30 atmospheres are reported between 20 and 50° for benzene and toluene and between 20 and 40° for carbon tetrachloride, chloroform and *n*-heptane. From these are calculated, using thermal expansion coefficients derived from the "International Critical Tables," the corresponding specific heats. Since the calculated probable errors of these determinations are always below 0.1% and since it is not necessary to apply correction factors to the observed temperature and pressure differences, it is believed that they fix

¹¹ Shiba, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, **16**, 205 (1931).

the specific heats of the various liquids to better than 0.5%. The specific heats measured by previous investigators, although their mutual discordance makes a comparison difficult, are in fair agreement with those here reported.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

SOLID CADMIUM AMALGAMS. AN X-RAY PROOF OF THE COMPOUND Cd_3Hg

BY NELSON W. TAYLOR

RECEIVED MARCH 7, 1932

PUBLISHED JULY 6, 1932

The possible existence of a compound between cadmium and mercury has been a question of interest for many years. The evidence has been conflicting. If the thermodynamic activity of cadmium is defined as unity for the pure liquid, it is found for liquid cadmium amalgams that the ratio of activity to mole fraction for cadmium is less than unity over the whole concentration range. The same is true of mercury when the activity of pure liquid mercury is taken as unity. Hildebrand, Foster and Beebe¹ found that the vapor pressures of mercury over liquid cadmium amalgams at 323° were less than corresponded to the mole fraction; and Richards and Forbes,² who measured concentration cells of cadmium amalgams at room temperature, obtained electromotive force values too large. Both of these criteria indicate an affinity between the two components, which should be manifested in complex or compound formation.³

On the other hand, microscopic or thermal analyses of solid alloys of cadmium with mercury have hitherto not brought to light any compound. The constitution diagram, based largely on the work of Bijl and of Mehl and Barrett,⁴ shows three solid solutions but no compounds. The stability of any compound which may exist should certainly be greater in the solid than in the liquid state. As the evidence from electromotive force and vapor pressure data is quite trustworthy it was a matter of considerable interest to make an x-ray study of certain amalgam compositions which had not been thoroughly investigated.

R. F. Mehl⁵ made x-ray patterns of ten alloys of Cd-Hg and reported that those containing more than 60 weight per cent. (73 atomic per cent.)

¹ Hildebrand, Foster and Beebe, *THIS JOURNAL*, **42**, 545 (1920).

² Richards and Forbes, *Carnegie Instit. Pub. No. 56* (1906).

³ The causes of deviations from ideal solution behavior are given detailed treatment in J. H. Hildebrand, "Solubility," The Chemical Catalog Company, New York, 1924, and in recent journal articles by Professor Hildebrand.

⁴ Bijl, *Z. physik. Chem.*, **41**, 641 (1902). Mehl and Barrett, *A. I. M. M. E. Tech. Pub. No. 225* (1929).

⁵ Mehl, *THIS JOURNAL*, **50**, 381 (1928).